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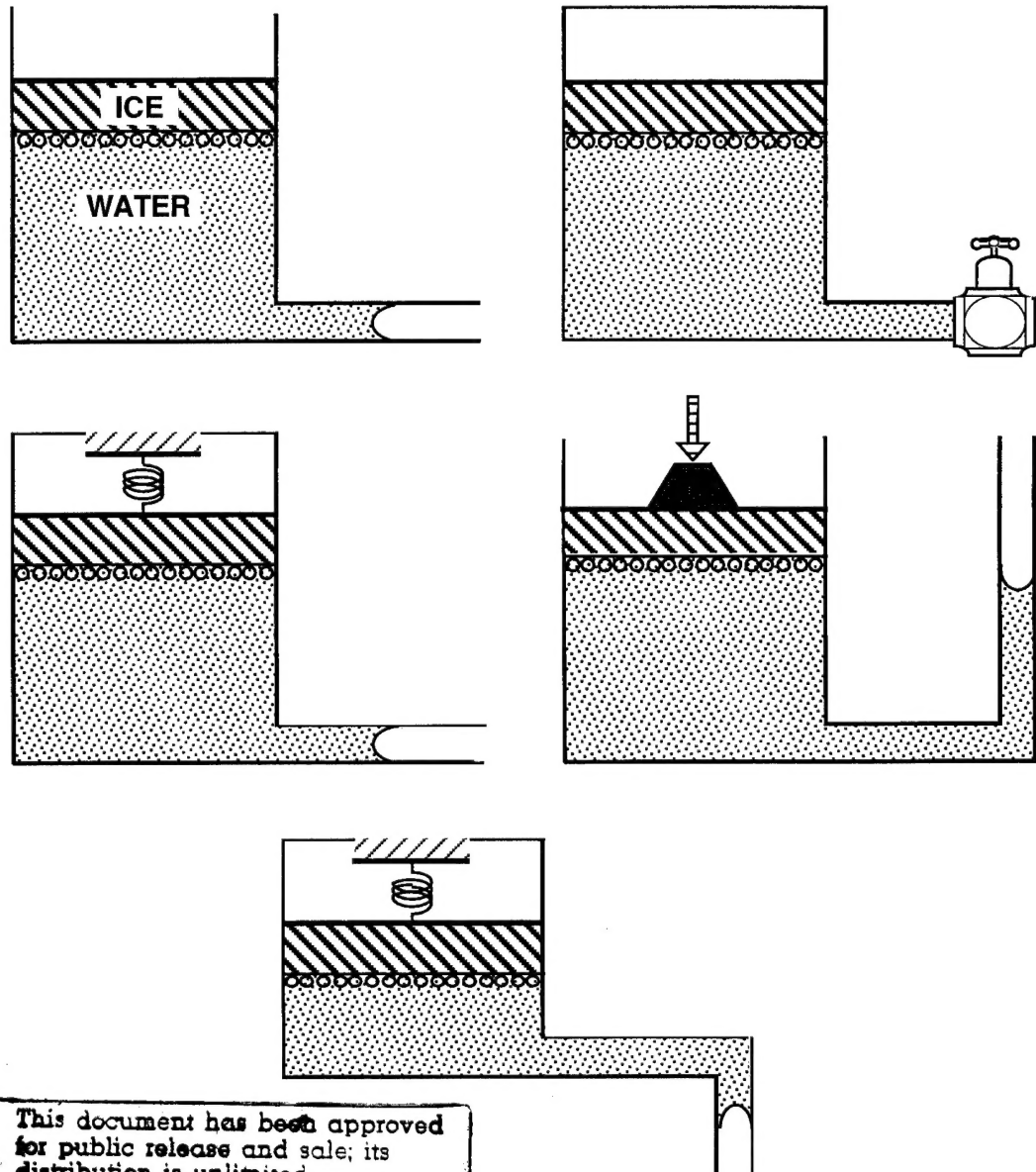
CRREL REPORT



Applications of the Clapeyron Equation to Water and Ice in Porous Media

Patrick B. Black

March 1995



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Abstract

The equilibrium condition for water and ice in an air-free porous medium is presented. The equation of state for this system is the Clapeyron equation. This equation is presented in a general form that explicitly shows the pressure-difference dependence with temperature for water and ice. Five solution scenarios are then discussed in terms of applicability to porous media.

Cover: Representation of the five solutions of the Clapeyron equation.

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.



**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

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PREFACE

This report was prepared by Patrick B. Black, Soil Physicist, Applied Research Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the Office of the Chief of Engineers under DA Project 4A762784AT42, *Design, Construction and Operations Technology for Cold Regions*, Task CP, Work Unit C01, *Freezing and Thawing of Soil Water Systems*. Samuel Colbeck, Edward Arons and David Cate provided technical reviews of this report.

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Applications of the Clapeyron Equation to Water and Ice in Porous Media

PATRICK B. BLACK

INTRODUCTION

Quantifying the relationship between water and ice in a porous medium has been a subject of interest for many years. Hudson (1906) first discussed possible applications of the Clapeyron equation to water and ice subjected to different pressure conditions for a given temperature change. Much later, Edlefsen and Anderson (1943) extended Hudson's analysis to the phase equilibrium condition of water and ice in soil. In both cases, they approached the problem from an equilibrium thermodynamic assumption that included a steady-state framework that did not include the flow of water.

This report extends the traditional application of the Clapeyron equation to include mass flow in ice-containing porous media. It is not intended to serve as an introduction to equilibrium thermodynamics for porous media. There are many other references that discuss that topic, and some are cited below. Instead, it is intended to explore the use of phase equilibrium concepts for modeling heat and mass transport in air-free, ice-containing porous media.

CONDITIONS AT EQUILIBRIUM

The system of interest in the study of freezing in a porous material is shown in Figure 1. It consists of a porous material with water in two phases: ice and liquid. Furthermore, it is assumed that any liquid water in the system will always be located between the surface of the porous matrix and the ice. There is ample justification for the existence and this configuration of the liquid film. One group of theories attributes the film to an adsorption force emanating from the surface of the porous medium (Miller 1980), while another group attributes the origin of the film to a liquid transition layer on the ice (Cahn et al. 1992). The result of this behavior is that we can treat the porous me-

dium as "inert" and need not include it as a separate chemical component.

The starting point for phase equilibrium thermodynamics is the Gibbs equation. This equation expresses the chemical potential μ for a phase. This results in two equations for a two-phase system consisting of liquid water w and ice i :

$$\begin{aligned}\mu_w &= V_w dp_w - S_w dT \\ \mu_i &= V_i dp_i - S_i dT\end{aligned}\quad (1)$$

in which V and S are molar volume and entropy, and p and T are absolute pressure and temperature. The equilibrium condition ($d\mu = 0$) for liquid water and ice is obtained when the chemical potentials are equal ($\mu_w = \mu_i$). This condition results in the Clapeyron equation:

$$V_w dp_w - V_i dp_i = (S_w - S_i) dT = \frac{\Delta H_{wi}}{T_0} dT \quad (2)$$

in which ΔH is the molar heat of fusion at T_0 (273.15 K), the standard melting temperature of a planar surface of ice.

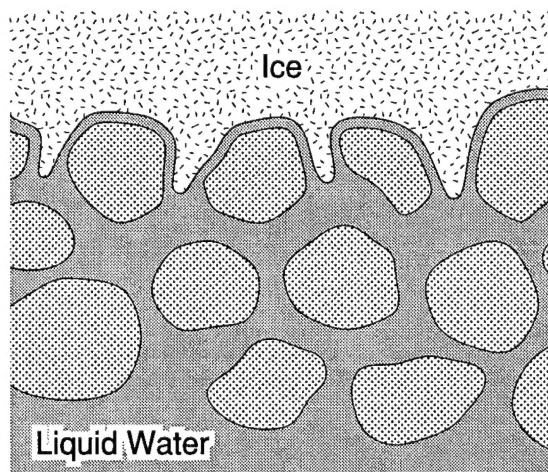


Figure 1. Ice-water configuration surrounding a porous medium.

The temperature and pressure units are usually changed to make the Clapeyron equation more functional in experimental applications. First, temperature is expressed in terms of the Celsius scale:

$$\theta = T - T_0. \quad (3)$$

Next, the pressures are expressed as gauge pressure by referencing to atmospheric pressure p_0 :

$$u = p - p_0. \quad (4)$$

Finally, the specific gravity of ice γ_i (0.917) and the volumetric latent heat of fusion h (Mg/m³) are defined as

$$\gamma_i = \frac{V_i}{V_w} \quad (5)$$

and

$$h = \frac{\Delta H_{wi}}{V_w}.$$

These substitutions result in the differential form of the so-called generalized Clapeyron equation:

$$du_w - \frac{du_i}{\gamma_i} = \frac{h}{T_0} d\theta. \quad (6)$$

Relationships similar to the Clapeyron equation have a history of use in ice-bearing porous media. In the second decade of this century, Bouyoucos and McCool (1916) measured the freezing point depression of soil-water systems at various degrees of saturation as a method of inferring the pressure of bound water. In the 1930s Schofield (1935) also used the freezing point depression approach to quantify the moisture tension of low-water-content soils. This type of work was of questionable use since the results appeared to work sometimes but fail many times. Edlefsen and Anderson attempted to develop a comprehensive theory of soil moisture in their classic monograph in 1943 in which they developed and then discussed the Clapeyron equation for soil-water systems. This report will closely follow their discussion and add some interpretation. It is interesting to note that they referred to eq 2 and 6 as the Clausius-Clapeyron equation. This is not correct; the Clausius-Clapeyron equation applies to liquid-vapor equilibrium, whereas the Clapeyron equation refers to any equilibrium phase composition.

It should be noted that u_w is the hydrostatic pressure of pure liquid water. If there are any impurities in solution, the water pressure must be

adjusted. This is conveniently performed by subtracting an osmotic pressure that is calculated for a dilute solution by the van't Hoff's equation (Castellan 1971). For the purpose of this report, it is assumed that there are no impurities, so that an osmotic pressure term is not required in eq 6. Similarly the ice phase might also contain trapped impurities that must be included in the expression for the ice pressure. This case will also be excluded by assuming the ice to be pure.

Inspection of eq 6 reveals that there are three unknowns (u_w , u_i and θ) and one equation. Equilibrium is therefore described when eq 6 is integrated and two of the variables are given. Another method to determine the number of intensive variables F required to describe the state of a system in equilibrium is Gibb's phase rule for a flat interface, which states that (Castellan 1971)

$$F = C - P + 2 \quad (7)$$

in which C is the number of components and P is the number of phases. There are no chemical reactions in this example. This predicts that only one intensive variable is required to fix the equilibrium condition for the case of water and two phases. But the system depicted in Figure 1 has an additional degree of freedom arising from the curvature, which results in a pressure difference between the liquid water and the ice. Thus, two intensive variables are required to describe a single-component, two-phase system with curvature.

Five physically significant scenarios are applicable to eq 6, and each will give a different quantitative prediction of the pressure-temperature relationship. Hudson (1906) and Edlefsen and Anderson (1943) obtained four solution classes by constraining one or both of the pressures or the temperature. This approach reduces the number of intensive variables required to describe the equilibrium condition. The final case treats the system in terms of the pressure difference between the two phases. The particular choice will depend on the prevailing environmental constraints on the system under study.

APPLICATIONS OF THE CLAPEYRON EQUATION

Figure 2 depicts the experimental setup of Miller et al. (1960). In this experiment they were able to subject the isothermal system to incremental

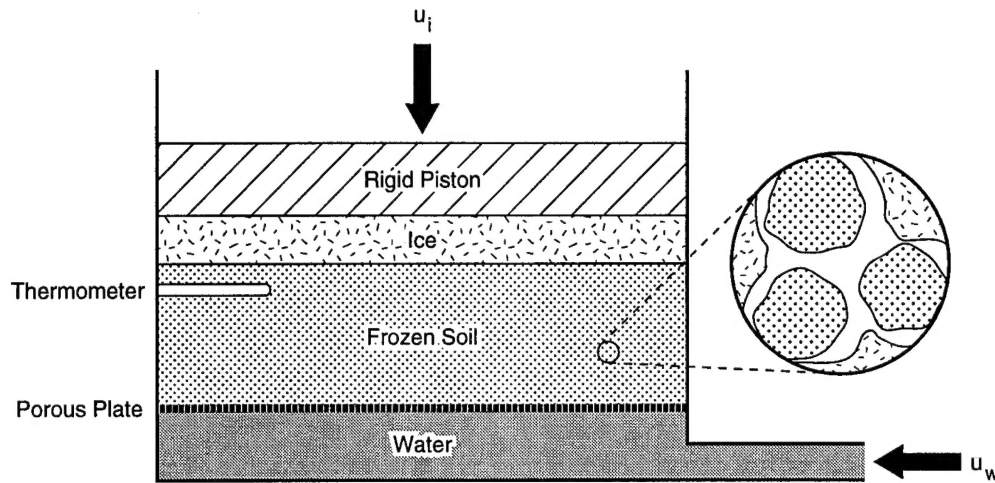


Figure 2. Schematic representation of the Miller et al. (1960) experiment.

changes in ice or water pressures and monitor the resulting change in temperature in the soil. In the apparatus the liquid water in the soil is in hydraulic contact with the water in the lower horizontal tube. The water pressure in that tube is therefore the pressure of the water in the soil. Similarly the pressure of the ice above the soil is the same as the pressure of the ice in the soil, since it too is mutually connected.

Case 1: $d\theta = f(du_i, du_w); du_i = du_w$

This is the standard textbook example for bulk solutions. It was first developed in the 1850s by Thompson for the freezing point depression of bulk solutions subjected to equal pressure changes on the ice and water phases. In this case, $u_i = u_w$ in Figure 2. The pressure-temperature behavior is

$$d\theta = f(du_i = du_w = dU) \quad (8)$$

$$\frac{dU}{d\theta} = \frac{h\gamma_i}{T_0} \frac{1}{\gamma_i - 1}$$

$$= -13.49 \text{ MPa}/^\circ\text{C} \quad \text{or} \\ = -0.074^\circ\text{C}/\text{MPa}.$$

This equation predicts a 0.074°C lowering of the melting temperature for a 1-MPa increase in confining pressure on both the ice and the liquid water phases. While this seems to be a very small change in temperature, the inverse view is that there is a very large change in pressure for a small change in temperature.

This situation might apply to porous media that

are purely colloidal, supersaturated with water, or consisting of large grains with a low unfrozen water content. When the system is supersaturated with water or is essentially a colloidal suspension of water, surface tension and curvature effects are not important. The pressures of the liquid water and ice are therefore essentially equal. This can happen to the water in the surface soil that undergoes freezing to shallow depths so that there is no confining pressure on the ice. This is also possible in pure clay soils. When the porous medium is composed of large grains and the unfrozen film is thin, then the radius of curvature at the ice-water interface is so small compared to the film thickness that it is closely approximated as a flat surface with equal liquid and ice pressures.

Case 2: $d\theta = 0 = f(du_i, du_w)$

$$\begin{aligned} \frac{du_w}{du_i} &= \frac{1}{\gamma_i} \\ &= 1.09. \end{aligned} \quad (9)$$

This example happens under the unique condition that the curvature between the two phases remains constant for a given temperature. While this condition is of academic interest, it is of little significance in environmentally important porous media like soil-water systems. It just states that the melting temperature remains constant if the change in confining pressure on the water is 1.09 times greater than the change in the ice pressure.

Once some ice is formed and then the volume of liquid water and ice are fixed in Figure 2, the measured pressure changes with temperature

would follow eq 9. This might be approximated in a soil system in which there is a volume of frozen soil surrounded by rigid and impermeable walls.

Case 3: $d\theta = f(du_w, du_i); u_w = \text{constant}$

$$\begin{aligned} \frac{du_i}{d\theta} &= \frac{-h\gamma_i}{T_0} \\ &= -1.12 \text{ MPa/}^\circ\text{C} \\ &= -0.893^\circ\text{C/MPa.} \end{aligned} \quad (10)$$

This expression also predicts a lowering of the melting temperature of ice, but the change is greater by an order of magnitude than predicted by eq 8. On the other hand, there is an order-of-magnitude smaller increase in pressure for an equal lowering of temperature when compared to eq 6.

In this case the ice pressure is free to vary with temperature, while the liquid water pressure in Figure 2 remains constant. This condition was used by Koopmans and Miller (1966) to infer the ice pressure change with temperature in their tests, which measured changes in unfrozen water content with changes in temperature. By applying eq 10 to their data, along with the assumption that the geometry of the ice-water interface is the same as an air-water interface at the same water content, they obtained agreement with corresponding ice-free data for unsaturated soil by suitable adjustment for ice-water and air-water surface tensions (see eq 12).

Case 4: $d\theta = f(du_w, du_i); u_i = \text{constant}$

$$\begin{aligned} \frac{du_w}{d\theta} &= \frac{h}{T_0} \\ &= +1.22 \text{ MPa/}^\circ\text{C} \\ &= +0.819^\circ\text{C/MPa.} \end{aligned} \quad (11)$$

The pressure-temperature behavior when the ice pressure remains constant is of the same order of change as when the water pressure remained constant, but of opposite sign. This behavior was recognized by Hudson (1906) and later used by Schofield (1935) in his freezing point depression measurements. The positive sign now means that a *decrease* in liquid water pressure will result in a lowering of the melting temperature.

This is a common form used by many modelers. Unfortunately it is not as applicable as they infer. Again, soil near the surface that lacks any overburden but has a water table beneath the surface is described by eq 11. This indicates that the lower

the temperature, the greater the tension on the liquid water.

Case 5: $d\theta \neq 0 \neq f(du_i, du_w)$

Colbeck (1985) made direct observations of the curved interface between the ice and the liquid water in partially frozen porous media, just as depicted in Figures 1 and 2. These observations, along with his earlier images for partially frozen unsaturated porous media (1982), also showed the curvature to decrease with decreasing temperature. In terms of the Laplace surface tension equation, a decrease in the mean radius of curvature r indicates an increase in the pressure difference between the two phases:

$$u_i - u_w = \frac{2\sigma_{iw}}{r} \quad (12)$$

in which σ_{iw} is the ice-water surface tension. The earlier experiments also revealed that the curvature of the water-air interface indicated that the liquid water pressure was always less than atmospheric, while the observed ice-air curvature indicated that the ice pressure was always greater than atmospheric. It is difficult to determine which constraint is required ($u_w = \text{constant}$ or $u_i = \text{constant}$) to use the Clapeyron equation to describe the behavior in these experiments. What is clear is that the curvature, and therefore the pressure difference between the two phases, is a function of temperature. To emphasize that this is a relationship for pressure difference between liquid water and ice, it is convenient to introduce a variable that is the difference:

$$\phi = u_i - u_w. \quad (13)$$

Substituting this expression into eq 6 results in two possible expressions, one in which the water pressure is an explicit variable and the other in which the ice pressure is the explicit variable:

$$d\phi = (\gamma_i - 1)du_w - \frac{h\gamma_i}{T_0}d\theta \quad (14)$$

$$d\phi = \left(1 - \frac{1}{\gamma_i}\right)du_i - \frac{h}{T_0}d\theta.$$

In the former case, if the water pressure is assumed to be constant, eq 10 is obtained. Similarly, if ice

pressure is constant in the latter case, then eq 11 is obtained.

There are at least three advantages to using eq 14 that are not realized by eq 10 and 11. First, eq 10 and 11 require that the pressure of one of the phases must remain constant with change in temperature. The observations of Colbeck do not show this to happen. Second, the pressure difference form of eq 14 is a logical analog to the pressure difference form used to model the water content of ice-free unsaturated soil (Koopmans and Miller 1966). Third, as will be discussed, eq 14 gives a simple explanation for the observed behavior of liquid water flow into and out of the frozen fringe during the formation of ice lenses.

DISCUSSION

The pressure-temperature behavior of liquid water and ice is used to model material properties of, and heat and mass transport through, porous media. Traditional material properties such as unfrozen water content and hydraulic conductivity are usually expressed as functions of temperature, while thermal conductivity and stress behavior are presented as functions of unfrozen water content. These properties are then used in models for mass and energy transport. It was shown above that temperature alone is not always sufficient to completely specify the conditions at equilibrium. Instead of using temperature, it is more reasonable to express the material properties as functions of ϕ . Unfrozen water content can also be expressed as a function of ϕ (Black and Tice 1989). Thus, all material properties for frozen soil are functions of the pressure difference between the ice and water phases ϕ .

For example, unfrozen water content data that are collected as function of temperature are transformed into functions of ϕ by using eq 14, which has two forms. The correct form depends on the experimental method. In a constant-stress device that has direct hydraulic connection to the atmosphere, the first form is used, with u_w set to its value of zero (Black and Miller 1990). When the data are collected in an unconstrained manner, then there is uncertainty as to the magnitude of either phase pressure. In this case, a band of uncertainty is obtained by using both forms of eq 14, with the explicit pressure set to zero (Black and Tice 1989, Black 1991). Finally, modeling ground freezing then proceeds in terms of ϕ , and the form

of eq 14 employed depends on the environmental conditions.

An example is the modeling of mass transport through a frozen fringe, shown in Figure 3. This is the zone of partially frozen soil bounded by an ice lens on the cold side and unfrozen soil on the warm side. Black and Miller (1990) assumed that u_w at the base of the fringe was known (perhaps it is zero), so that the former form of eq 14 was used (Black and Miller 1990). They then calculated the required liquid water pressure gradient at the base of the fringe for given boundary conditions and were able to start an iterative process to calculate pressures of liquid water and ice throughout the fringe.

Additional insight into the observed behavior of ice and water flux in heaving soil is obtained from eq 14. Forland and Ratkje (1980) contended that the Clapeyron equation does not apply to transport through the frozen fringe. They believed that under the condition of restricted growth of an ice lens (Radd and Oertle 1973), the Clapeyron equation would predict a pressure gradient of liquid water in reaction to a temperature gradient across the fringe. This, they believed, was not physically possible because it would induce a flux of water. With no growth of a lens or penetration of the fringe, there was no sink for a flux of water. As a result they abandoned equilibrium thermodynamics and chose the route of irreversible thermodynamics.

It is not that the Clapeyron equation does not apply to the frozen fringe, it is that their interpre-

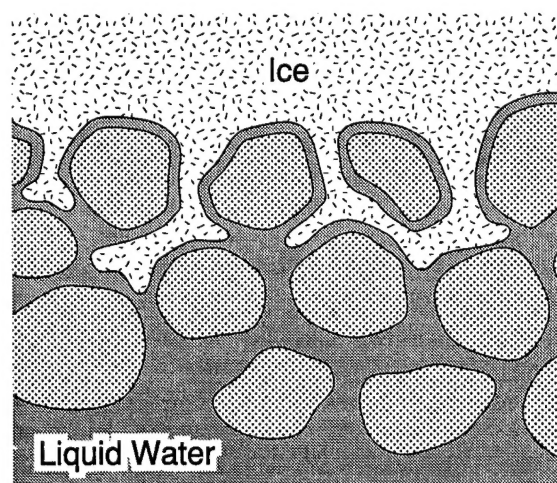


Figure 3. Representation of the frozen fringe.

tation does not apply. They implicitly assumed that the ice pressure was constant, as in eq 11. Therefore, a temperature gradient must be balanced by a pressure gradient in the liquid water. The correct interpretation is given by eq 14. In this case, there is balance between the liquid water and ice pressures. A fixed temperature gradient results in a fixed gradient of ϕ . Now, as a confining load on top of the ice lens increases and its growth decreases, there is a corresponding decrease in the flux of water to the ice lens. This results in a decreased pressure gradient in the liquid water, which is made up by an increased ice pressure gradient to keep a constant gradient of ϕ for a constant temperature gradient. In the extreme case when there is no ice lens growth, the liquid water pressure gradient is zero because the ice phase is maintaining the necessary pressure gradient for equilibrium.

Another observation from frost heave is the discharge of liquid water out of the frozen fringe into the unfrozen soil as both penetration of the fringe and growth of the ice lens occur. This is readily explained by the Clapeyron equation. These conditions generally occur at the onset of heaving, when the gradients are severe. The rapid ice penetration and slight growth of the ice lens results in an overabundance of liquid water in the fringe due to the density change from liquid to ice. The excess liquid not required to feed ice lens growth results in a liquid water pressure gradient directed towards the unfrozen soil and in the direction of increasing temperature. Equilibrium is maintained by a corresponding increase in the ice pressure gradient. The resulting large ice pressure gradients also cause large gradients in neutral stress, which result in rapid changes in the location for optimum ice lens growth. This is shown by the close spacing and small sizes of ice lenses under these conditions (O'Neill and Miller 1985, Black and Miller 1990).

CONCLUSIONS

The water and ice contained within a porous medium do not necessarily exhibit the same behavior as the same water and ice in bulk. The most important difference is that the geometric restrictions imposed by porous media lead to curved interfaces separating the ice and water phases. The presence of a curved interface indicates that the pressures of the two phases are different. How

they differ depends on the environmental conditions that are imposed on the system. The discussion presented in this report should help interpret and model the behavior of water and ice in freezing porous media.

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